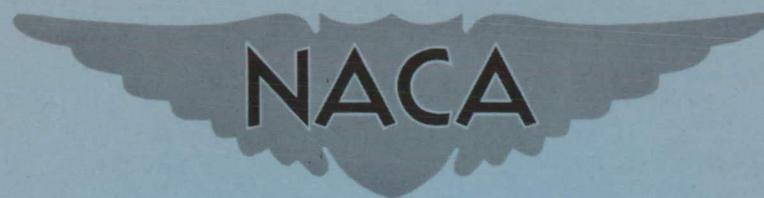


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RESEARCH MEMORANDUM

PREPARATION OF DIPENTABORYLMETHANE BY FRIEDEL-

CRAFTS REACTION

By Albert C. Antoine

Lewis Flight Propulsion Laboratory
Cleveland, Ohio

CANCELLED

Classification

CHANGED TO Uncl.By authority of NASA TRA #45 5/14/61Changed by AKZ Date JUN 14 1981

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NATIONAL ADVISORY COMMITTEE
FOR AERONAUTICS

WASHINGTON

April 1, 1958

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RESEARCH MEMORANDUM

PREPARATION OF DIPENTABORYLMETHANE BY FRIEDEL-CRAFTS REACTION

By Albert C. Antoine

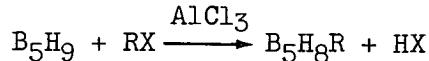
SUMMARY

Preparation of dipentaborylmethane by reacting pentaborane with dichloromethane in the presence of aluminum chloride gave maximum yields of less than 1 percent. No dipentaborylethane resulted from the reaction of pentaborane with 1,2-dichloroethane and with 1,2-dibromoethane. The reaction did produce ethylpentaborane in yields up to 47 percent. The formation of polymeric solids accompanied all reactions. These solids resulted in part from the decomposition of unstable reaction products, one of which was isolated but not identified.

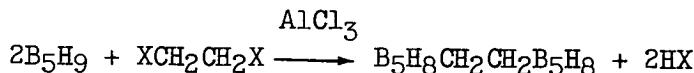
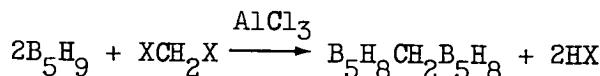
INTRODUCTION

Boron hydrides are of great interest in the current search for new high-energy fuels. Two characteristics of boron hydrides present serious problems in their use as fuels: their ready flammability on exposure to air and their extreme toxicity. Alkyl derivatives of boron hydrides hold promise of reduced toxicity and reduced flammability on exposure to air while retaining high heats of combustion (ref. 1).

Several alkyl derivatives of pentaborane have been prepared (refs. 2 to 4). They have generally been prepared by a Friedel-Crafts reaction with the boron hydride and alkyl halides. The general reaction is



where R is the alkyl group and X is the halide. The alkyl halides previously used have been the monohalogenated alkanes such as methyl, ethyl, and propyl chlorides, bromides, or iodides. The present report describes the reaction with five dihalogenated alkanes: dichloromethane, dibromomethane, diiodomethane, 1,2-dichloroethane, and 1,2-dibromoethane. The products expected would have two pentaboryl groups in one molecule. The general reaction is



The heats of combustion are expected to compare favorably with those of the other alkyl derivatives (ref. 1).

APPARATUS AND PROCEDURE

The pentaborane was used as obtained from the manufacturer, since periodic checks of the vapor pressure showed little change. The alkyl halides were commercial products. They were dried over anhydrous calcium sulfate for 24 hours prior to use.

Reactions of Pentaborane with Dichloromethane

All reactions were carried out in a dry box. The solvent *n*-heptane was placed in a flask and aluminum chloride, pentaborane, and dichloromethane were added in that order. The mixture was refluxed for 5 hours. After cooling, the volatile material was removed under vacuum and the residue extracted with carbon disulfide. An amorphous material was left after removal of the carbon disulfide. When this material was heated in a sublimation apparatus, a colorless crystalline material resulted. The crystals were washed with water, then recrystallized from carbon disulfide. The melting point, 51.5° to 53.0° C, was determined in a double-bath melting-point apparatus (ref. 5). Elemental analysis gave the following results: Percent boron, 78.9; percent carbon, 8.4; percent hydrogen, 13.5. The calculated results for dipentaborylmethane are: Percent boron, 78.2; percent carbon, 8.7; percent hydrogen, 13.1. Figure 1 shows the infrared spectrum of the product. The yield was 0.35 percent.

Aluminum chloride and aluminum (20-mesh) were placed in a flask. Dichloromethane and pentaborane were added in succession. The mixture was refluxed for 4 hours. After cooling, volatile material was removed by vacuum distillation at room temperature and 20 millimeters of mercury. A second fraction was removed by boiling from 35° to 50° C at 1 to 2 millimeters of mercury. This fraction was redistilled yielding material whose boiling point was 50° C at 7 millimeters of mercury. The product was spontaneously flammable in air and readily decomposed at room temperature in a nitrogen atmosphere. Elemental analysis showed that the compound contained chlorine in addition to boron, carbon, and hydrogen. The infrared spectrum is shown in figure 2.

Reaction of Pentaborane with Dibromomethane

and with Diiodomethane

Pentaborane was reacted with dibromomethane and with diiodomethane in the presence of aluminum chloride with *n*-heptane as the solvent. The reactions were carried out in a manner similar to that used with dichloromethane. Small amounts of an alkylated boron hydride were indicated by infrared spectra, but no product was isolated.

Reaction of Pentaborane with 1,2-Dibromoethane

Aluminum chloride and 1,2-dibromoethane were added to *n*-decane in a flask. The flask was shaken as pentaborane was slowly added. The flask was then slowly heated because a vigorous reaction occurs shortly after heating begins. The mixture was refluxed for 7 hours. Unreacted pentaborane was removed from the reaction mixture by distillation, and the remaining liquid was distilled under vacuum. A fraction boiling from 35° to 63° C at 19 to 20 millimeters of mercury was collected, introduced into a vacuum system (ref. 6), and fractionated. A product having a vapor pressure of 15 millimeters at 0° C, 35 millimeters at 25° C was isolated. The molecular weight was determined from the weight and volume of a sample of vapor and found to be 95.76. The literature values for ethylpentaborane are: vapor pressure, 13 millimeters at 0° C, 40 millimeters at 25°; molecular weight, 94.0 (ref. 2). The infrared spectrum of the product is shown in figure 3.

Reaction of Pentaborane with 1,2-Dichloroethane

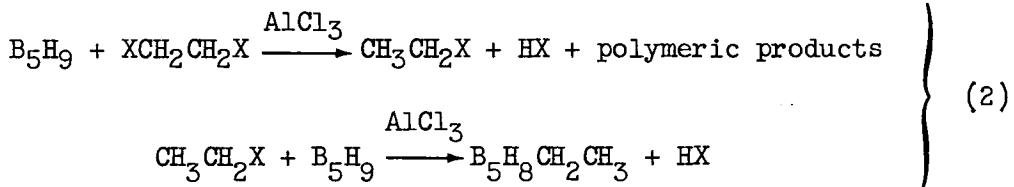
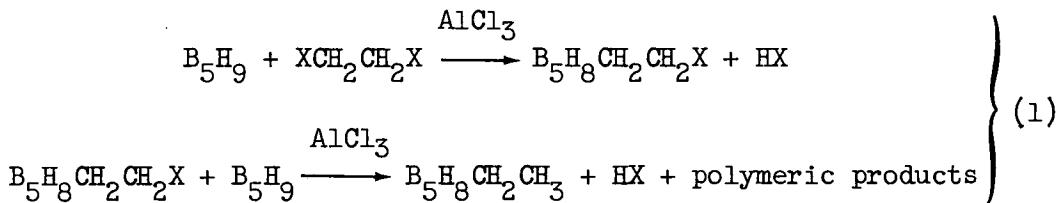
Aluminum chloride and 1,2-dichloroethane were placed in a flask. The flask was shaken as pentaborane was added in small portions. A moderately vigorous reaction started soon after heating began but subsided in a few minutes. The mixture was refluxed for 6 hours. Fractionation of the reaction mixture yielded pentaborane and ethylpentaborane.

RESULTS AND DISCUSSION

Dipentaborylmethane was formed in very small quantities by the reaction of pentaborane with dichloromethane. Varying amounts of the reactants were recovered, together with a polymeric solid material formed from direct decomposition of the reactants, or from decomposition of the reaction products, or from a combination of the two processes. These results are summarized in table I. Dibromomethane and diiodomethane were reacted under like conditions. None of the desired product was isolated, although infrared analysis indicated the presence of some alkylated boron hydride. (See table II.)

Reacting dichloromethane without a solvent and in the presence of aluminum did not improve the yield of dipentaborylmethane. However, an unstable liquid compound containing chlorine was also formed. Molecular-weight determinations and boron analyses indicated that the compound contained fewer than five boron atoms, rather than the pentaborane structure. In experiments with diiodomethane under similar conditions, a like compound was observed by infrared spectra (fig. 4) but was not isolated.

Reacting 1,2-dichloroethane and 1,2-dibromoethane with pentaborane yielded no disubstituted ethane. Instead, ethylpentaborane was the only product isolated, as indicated in table III. Similar behavior has been observed in the reaction of decaborane with 1,2-dichloroethane (ref. 7). The product obtained, ethylpentaborane, could arise in two ways, both of which involve a reduction by the hydride. The first method would begin with a Friedel-Crafts reaction with pentaborane and the dihalide, followed by reduction of the product. In the second method, the dihalide is reduced to the monohalide and the latter then reacts with pentaborane. The equations for the two processes are:



SUMMARY OF RESULTS

1. Yields of less than 1 percent of dipentaborylmethane were obtained from a Friedel-Crafts reaction between pentaborane and dichloromethane. Using dibromomethane and diiodomethane in place of dichloromethane did not improve the yield.
2. None of the desired product was obtained from the reactions of pentaborane with 1,2-dichloroethane and 1,2-dibromoethane. Ethylpentaborane was obtained, with a maximum yield of 47 percent.

3. The formation of polymeric solids accompanied all reactions, partly as a result of the decomposition of unstable reaction products. One such compound was isolated but not identified.

Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, January 16, 1958.

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TABLE I. - SUMMARY OF REACTIONS OF PENTABORANE WITH DICHLOROMETHANE

Reactants, moles		Solvent, n-heptane, mL	Time, hr	Reactants recovered, moles	Residue, percent weight of reactants	Product, B ₅ H ₈ CH ₂ B ₅ H ₈ , percent yield	Remarks
B ₅ H ₉	CH ₂ Cl ₂			B ₅ H ₉ CH ₂ Cl ₂			
0.42	0.25	200	43	0.08	---	24	Product observed, but decomposed during attempted isolation
0.82	0.42	----	16	0.40	0.12	24	0.06
0.36	0.19	80	6	0.22	0.09	<1	0.24
0.57	0.39	----	4.5	0.33	0.25	<1	0.36
							3 grams of a liquid product containing chlorine was isolated; the catalyst was a mixture of AlCl ₃ and 20% Al (by weight)

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TABLE II. - COMPARISON OF REACTIONS OF PENTABORANE WITH
DICHLOROMETHANE, DIBROMOMETHANE, AND DIIODOMETHANE
UNDER LIKE CONDITIONS

Reactants, moles		AlCl ₃ , moles	Solvent, n-heptane, ml	Time, hr	Product, B ₅ H ₈ CH ₂ B ₅ H ₈ , percent yield
B ₅ H ₉	Halide				
0.21	CH ₂ Cl ₂ , 0.12	0.023	30	4.5	0.35
0.29	CH ₂ Br ₂ , 0.12	0.026	30	5	(a)
0.29	CH ₂ I ₂ , 0.12	0.026	30	5	(a)

^aProduct observed in infrared spectra but not isolated.

TABLE III. - REACTION OF PENTABORANE WITH 1,2-DICHLOROETHANE
AND 1,2-DIBROMOETHANE

Reactants, moles		Solvent, n-decane, ml	Time, hr	Reactants recovered, moles		Residue, percent weight of reactants	Product, B ₅ H ₈ CH ₂ CH ₃ , percent yield
B ₅ H ₉	Halide			B ₅ H ₉	Halide		
0.27	ClCH ₂ CH ₂ Cl, 0.12	--	6	0.07	None	45	20
0.40	BrCH ₂ CH ₂ Br, 0.10	50	7	0.07	None	23	47

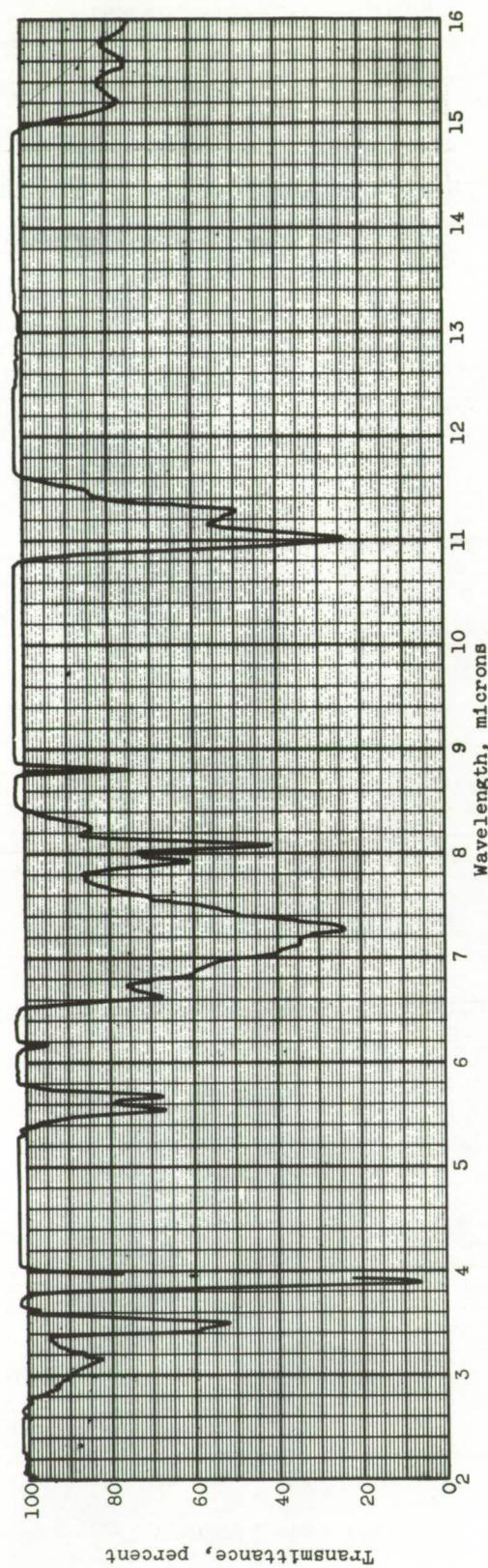


Figure 1. - Infrared spectrum of dipentaboronylmethane obtained from reaction of pentaborane with dichloromethane. Cell width, 0.1 millimeter; sample diluted 1:10 with carbon tetrachloride; pure carbon tetrachloride in reference cell.

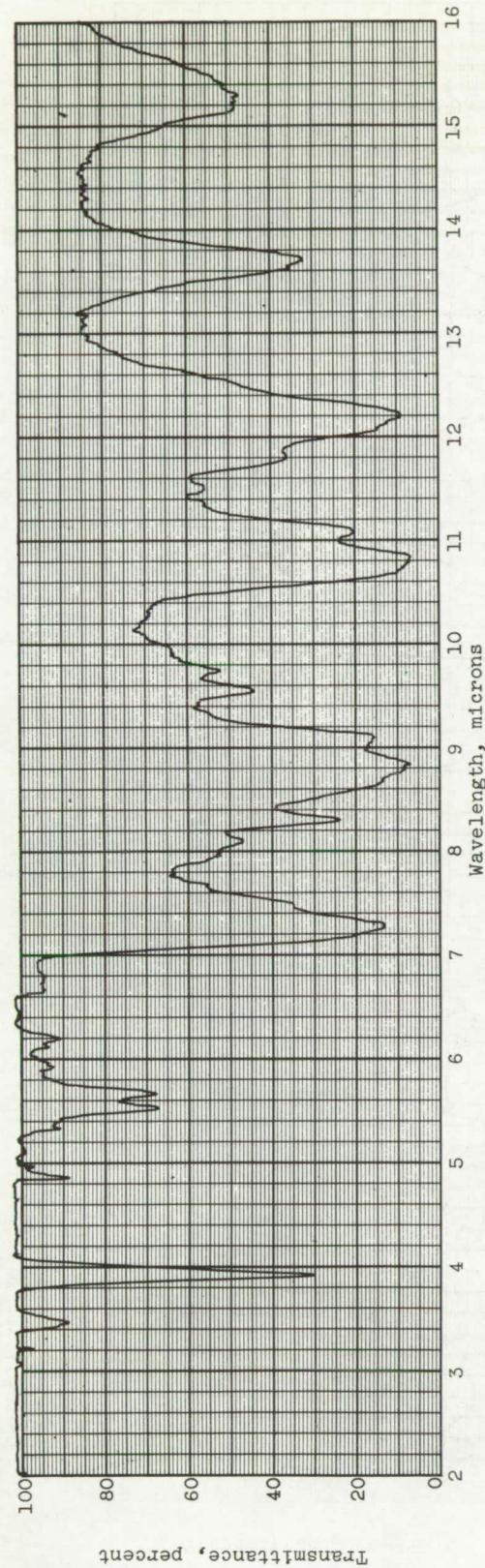


Figure 2. - Infrared spectrum of product of reaction of pentaborane with dichloromethane. Cell width, 0.1 millimeter; sample diluted about 1:10 with carbon disulfide; pure carbon disulfide in reference cell.

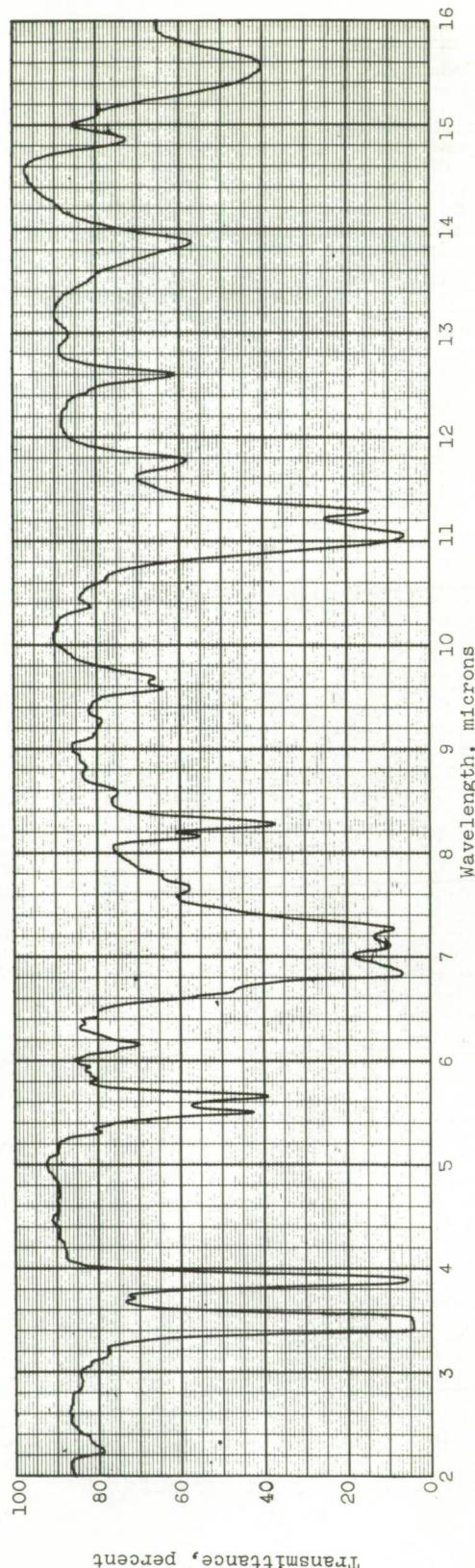


Figure 3. - Infrared spectrum of ethylenpentaborane obtained from reaction of pentaborane with 1,2-dibromoethane. Cell width, 0.06 millimeter; reference cell, sodium chloride.

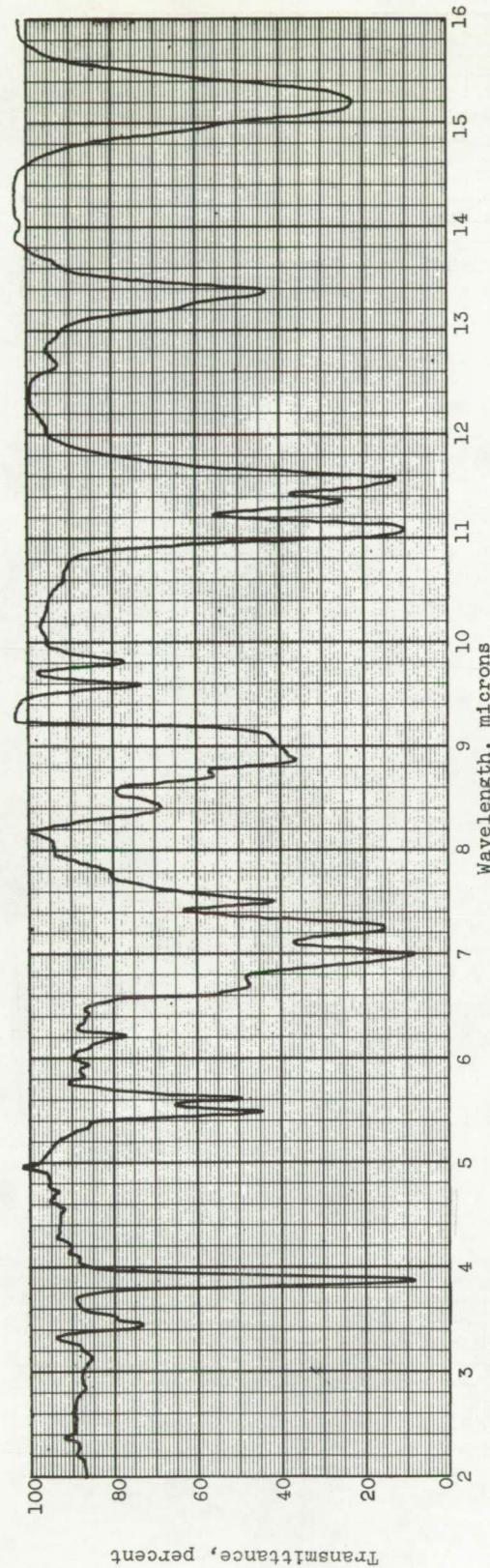


Figure 4. - Infrared spectrum of product of reaction of pentaborane with diiodomethane. Cell width, 0.1 millimeter; sample in diiodomethane; pure diiodomethane in reference cell.

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